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Citation: J. Chem. Phys. **126**, 191104 (2007); doi: 10.1063/1.2738059
View online: http://dx.doi.org/10.1063/1.2738059
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v126/i19
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Vapor-liquid coexistence in fluids of charged hard dumbbells

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(Received 20 March 2007; accepted 17 April 2007; published online 21 May 2007)

Vapor-liquid coexistence in fluids of charged hard dumbbells, each made up of two oppositely charged hard spheres with diameters σ and separation d, has been studied using grand-canonical Monte Carlo simulations. In the limit $d/\sigma \to 0$, and with the temperature scaled accordingly, the system corresponds to dipolar hard spheres. For separations in the range $0.3 < d/\sigma \leqslant 1$ the coexisting vapor phase contains compact clusters. For separations in the range $0.1 \leqslant d/\sigma < 0.3$ the coexistence is between a chainlike vapor and a networklike liquid. Finite-size effects preclude the simulation of the coexistence in systems with $d/\sigma < 0.1$, but extrapolations of the results to $d/\sigma \to 0$ yield estimates of the apparent critical parameters for dipolar hard spheres. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2738059]

In simple fluids with isotropic attractive interactions of sufficient range[1] the condensation transition occurs between a low-density vapor with high energy and high entropy and a high-density liquid with low energy and low entropy. Systems with strong dipolar interactions, however, seem to behave very differently. The Boltzmann-weighted, orientational average of the dipolar interaction potential has an isotropic, attractive, leading-order term proportional to $-1/r^6$ where r is the particle separation, and one might therefore anticipate that the condensation transition in such systems would be conventional.[2] Computer simulations show that at low temperatures the anisotropy and the long range of dipolar interactions give rise to extensive chainlike aggregation at low densities[3] and branched-network formation at high densities,[4] the primary structural signature being the nose-to-tail conformation of neighboring dipoles. It is unclear whether such association precludes any kind of fluid-fluid coexistence. For systems with Lennard-Jones (LJ) and dipolar interactions, Gibbs ensemble Monte Carlo (GEMC) simulations indicate that the vapor-liquid transition disappears when the strength of the isotropic $-1/r^6$ component of the LJ potential is reduced below a critical level.[5] This may be due to a failure of the GEMC technique; when particle aggregation is pronounced, the probability of transferring particles between two simulation boxes becomes extremely small. Recent canonical molecular dynamics simulations of the Stockmayer fluid suggest that coexistence occurs even with very high dipole moments,[6] while GEMC simulations of dipolar soft spheres (with no isotropic attraction) suggest that coexistence can only be observed with a threshold (electric or magnetic) field applied.[7] In the case of dipolar hard spheres (DHSs), earlier studies using GEMC and isothermal-isobaric MC simulations show no evidence of a transition,[8] but subsequent canonical, isothermal-isobaric, and grand-canonical MC studies[9] indicate that the isotherms under investigation were supercritical. Clearly, the situation is unresolved: for a recent review see Ref. 10.

In this Communication a new approach is made towards vapor-liquid coexistence in dipolar fluids by studying so-called charged hard dumbbells[11] (CHDs) with extensive MC simulations. Each CHD is made up of two oppositely charged hard spheres with diameters σ and charges $\pm q$, fused at a center-center distance d [see Fig. 1(a)]. When $d=\sigma$ the transition is very similar to that in the restricted primitive model (RPM) of ionic fluids;[12–14] in the RPM, oppositely charged ions associate at low temperature to form ion pairs that resemble CHDs.[11,15] As $d/\sigma \to 0$, and with the temperature scaled accordingly, the CHD model can be mapped on to DHSs with dipole moment $\mu = qd$. Hence, the CHD model provides a convenient bridge between "ionic" condensation (typified by the RPM, and CHDs with $d/\sigma = 1$) and pure dipolar condensation.

The ionic interaction potential is $q_i q_j / Dr$ where $D = 4\pi\epsilon_0$. Reduced units for the CHD model are as follows: ionic temperature $\tau^i = k_B T D\sigma / q^2$, "dipolar" temperature τ^d

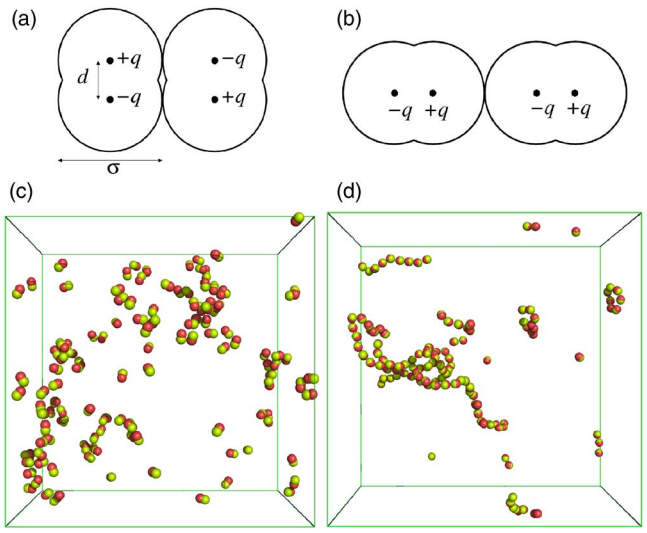

FIG. 1. (Color online) Configurations of CHDs: (a) side-by-side, antiparallel arrangement; (b) nose-to-tail, parallel arrangement; (c) vapor phase with $d/\sigma = 0.5$ at $\tau^d = 0.0777$ and $\rho^* = 0.0055$; and (d) vapor phase with $d/\sigma = 0.1$ at $\tau^d = 0.126$ and $\rho^* = 0.0035$.

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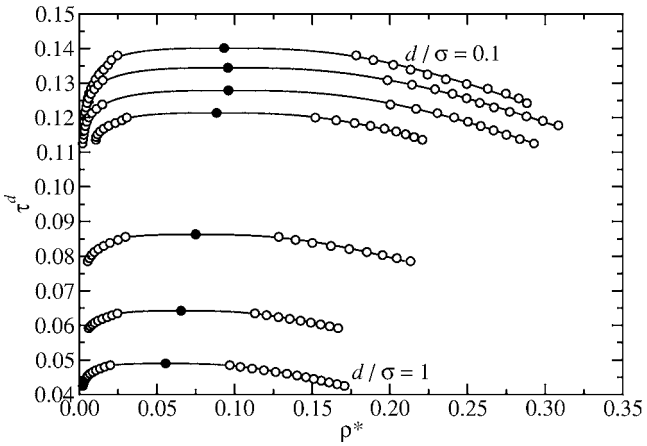

FIG. 2. Vapor-liquid coexistence curves for CHDs with, from top to bottom, d/σ=0.1, 0.15, 0.2, 0.25, 0.5, 0.75, and 1: (open symbols) GCMC simulation results; (lines) fits; and (filled symbols) fitted critical points.

$=k_BTD\sigma^3/\mu^2=\tau^i\sigma^2/d^2$, and reduced density $\rho^*=\rho\sigma^3$, where $\rho=N/V$ is the number of CHDs (N) in a volume V. Grand-canonical Monte Carlo (GCMC) simulations were performed using a cubic simulation cell with periodic boundary conditions applied. Coulomb interactions were evaluated using Ewald sums with conducting boundary conditions.[16] CHD translations and rotations were effected through attempted deletions and random insertions. Multicanonical preweighting was used to overcome the free-energy barrier separating coexisting phases; the weighting function $W(N)$ was iterated during each simulation to achieve a uniform sampling across the full range of density. Simulations at each state point consisted of between 10^9 and 10^{10} insertion/deletion attempts, and the particle number and configurational energy E were recorded at intervals of 100–500 such attempts. Histogram reweighting was used to combine data obtained with different chemical potentials and temperatures to form the joint probability distribution function $p(N,E)$ from which thermodynamic functions can be computed over the ranges of parameters sampled in the simulations. Coexisting phases were identified by equating the temperatures, chemical potentials, and pressures. The complete procedure (comprising multicanonical preweighting, histogram reweighting, and the determination of phase coexistence) was implemented as described in Ref. 17. The lengths of the simulations (total of ~2 CPU years) precluded a finite-size scaling study of the critical behavior, and so one system size (L/σ=12.5 or 13) was adopted for each value of d/σ. Estimates of the critical parameters were obtained by fitting the coexistence densities to the equation $\rho_\pm=\rho_c+At\pm Bt^\beta$, where ρ_c is the critical density, $t=|T-T_c|/T_c$, T_c is the critical temperature, and β =0.326 is the three-dimensional Ising order-parameter exponent.[24]

Coexistence curves in the ρ^*-τ^d plane are shown in Fig. 2. The results indicate that the condensation transition exists all the way down to almost purely dipolar hard particles (d=0.1σ). Beyond this point, the simulations became intractable due to the extent of aggregation. At low densities the simulations become trapped in sharp, local energy minima corresponding to configurations of system-spanning chains. This is a finite-size effect and it does not imply that condensation disappears for $d<0.1\sigma$. Alternative simulation methods may not improve the situation because the characteristic length scale in the fluid is comparable to the box length; the only cure may be to increase the box length by an order of magnitude.

TABLE I. Apparent critical parameters of the CHD fluid.

d/σ	L/σ	τ_c^i	τ_c^d	ρ_c^*
1	13	0.049 00(7)	0.049 00(7)	0.0556(2)
0.75	13	0.036 12(4)	0.064 22(8)	0.0655(1)
0.5	13	0.021 57(4)	0.086 3(2)	0.0749(5)
0.25	13	0.007 585(5)	0.121 36(7)	0.0885(9)
0.2	12.5	0.005 114(6)	0.127 9(1)	0.0960(9)
0.15	12.5	0.003 024(4)	0.134 4(2)	0.0958(8)
0.1	12.5	0.001 401(3)	0.140 1(3)	0.0933(8)

Critical parameters are summarized in Table I; the quoted uncertainties were taken from the fitting procedure only, and are therefore underestimates. The critical temperature and critical density at d/σ=1 are in good agreement with earlier finite-size scaling values of τ_c^i=0.049 11(3) and ρ_c^*=0.0505(15),[14] which justifies the simulation procedure. The results are also comparable to those for the RPM (Ref. 12) and a related "tethered dimer" fluid.[13] The CHD ionic critical temperature decreases with decreasing d because of the reduction in the dipole moment, but the dipolar critical temperature remains finite.

Figure 3(a) shows τ_c^d and ρ_c^* as functions of d/σ. As d/σ is decreased, the critical temperature increases monotonically and shows a linear dependence for $d/\sigma<0.3$. Fitting a straight line to the critical temperatures in the range d/σ <0.3 yields an apparent critical temperature for DHSs ($d/\sigma\to 0$) of $\tau_c^d\simeq 0.153\pm 0.001$. This is in surprisingly good agreement with the rough estimate of τ_c^d=0.15–0.16 made in

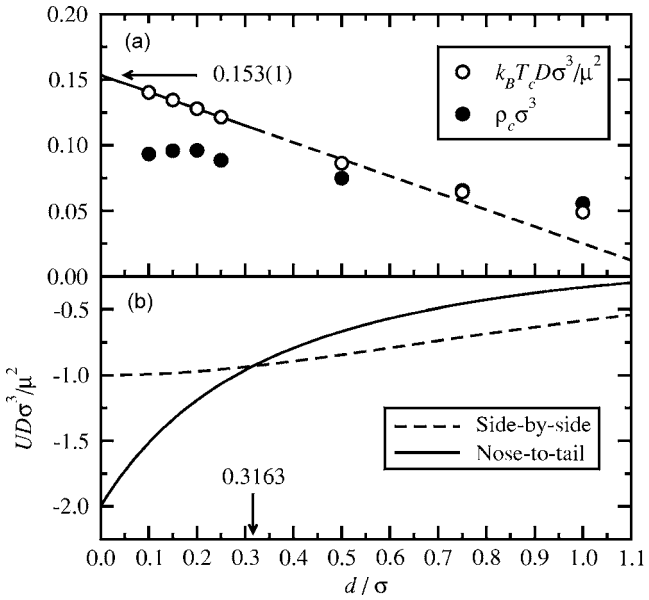

FIG. 3. (a) Critical temperature (open symbols) and critical density (filled symbols) for CHDs as functions of d/σ. The line is a linear fit to the critical temperatures for $0.1\leqslant d/\sigma<0.3$. (b) Interaction energy of two CHDs at contact in side-by-side antiparallel (dashed line) and nose-to-tail parallel (solid line) arrangements.

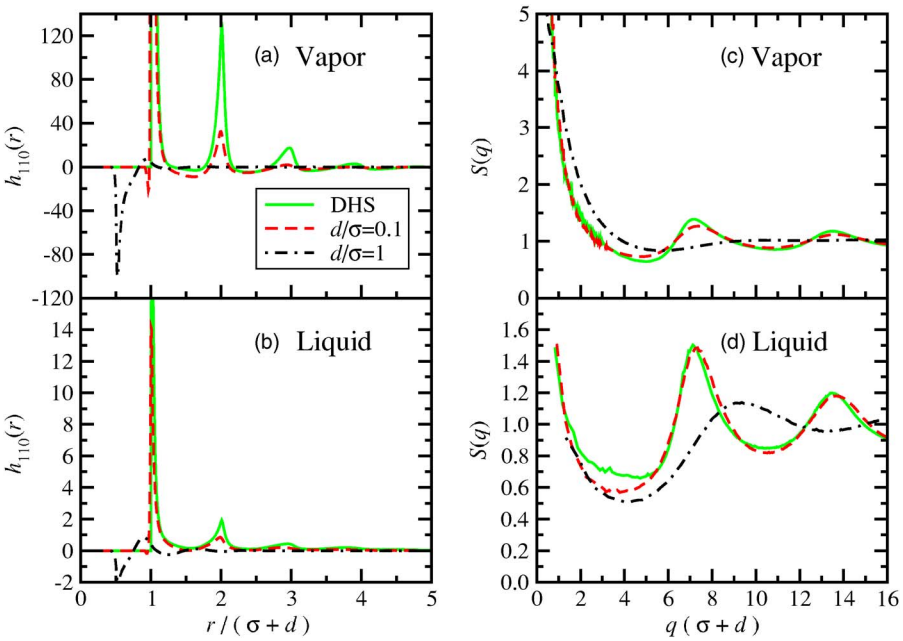

FIG. 4. (Color online) $h_{110}(r)$ and $S(q)$ in vapor and liquid phases near coexistence at relative temperature $0.9\tau_c^d$: (a) $h_{110}(r)$ in the vapor phase; (b) $h_{110}(r)$ in the liquid phase; (c) $S(q)$ in the vapor phase; and (d) $S(q)$ in the liquid phase. Systems and parameters: CHDs with $d/\sigma=1$, $\tau^d=0.0441$, $\rho^*_{\mathrm{vap}}=0.0040$, and $\rho^*_{\mathrm{liq}}=0.15$ (black dot-dashed lines); CHDs with $d/\sigma=0.1$, $\tau^d=0.126$, $\rho^*_{\mathrm{vap}}=0.0035$, and $\rho^*_{\mathrm{liq}}=0.30$ (red dashed lines); and DHSs, $\tau^d=0.138$, $\rho^*_{\mathrm{vap}}=0.0035$, and $\rho^*_{\mathrm{liq}}=0.30$ (green solid lines).

Ref. 9 (to our knowledge, no other reliable estimates are available). One might question whether this extrapolation is robust. Although it has not been possible to simulate coexisting phases of DHSs directly—due to the finite-size effects mentioned above—it would be remarkable if a new mechanism was to emerge in the narrow range $0<d/\sigma<0.1$ and prevent the transition. The apparent critical densities do not vary in a well-defined way, although these are notoriously difficult to determine accurately because of the flatness of the coexistence curves near the critical point. Nonetheless, a DHS critical density of $\rho_c^* \simeq 0.1$ seems reasonable.

The characteristics of condensation in the two regimes of $d/\sigma<0.3$ and $d/\sigma>0.3$ are different. It is useful to first compare the energies of two CHDs at contact in the antiparallel side-by-side and parallel nose-to-tail arrangements illustrated in Figs. 1(a) and 1(b), respectively. The energies are plotted in dipolar units in Fig. 3(b). The nose-to-tail conformation becomes energetically favorable over the side-by-side conformation when $d/\sigma<0.3163$. It might therefore be anticipated that when $d/\sigma \lesssim 0.3$ the condensation is dipolar and the coexisting phases contain extended chainlike aggregates, and when $d/\sigma>0.3$ the condensation is ionic in the sense that the coexisting phases contain more isolated compact clusters such as those in the RPM at coexistence.[15] This is indeed the case, as evidenced by Figs. 1(c) and 1(d) which show simulation snapshots of vapor phases near coexistence at relative temperature $0.9\tau_c^d$. With $d/\sigma=0.5$, the clusters are more compact and neighboring particles are preferentially aligned side by side. With $d/\sigma=0.1$, the vapor exhibits extensive chainlike aggregates. A similar crossover in cluster structure is apparent in fluids of dipolar hard spherocylinders and dumbbells as the hard-core aspect ratios are varied.[18,19]

The structures of the coexisting vapor and liquid phases are reflected in the correlation functions $h_{l_1 l_2 m}(r)$, these being the projections of the total correlation function, $h(\mathbf{r}_{12},\mathbf{e}_1,\mathbf{e}_2)$, on to rotational invariants.[20] Here, $\mathbf{r}_{12}$ is the center-center separation vector of two molecules, and $\mathbf{e}_i$ is the unit orientation vector on molecule i (parallel with its dipole vector). The function

$$h_{110}(r) = \frac{3\left\langle \Sigma_{i\neq j}^{N} \delta(|\mathbf{r}_{ij}|-r)\mathbf{e}_i\cdot\mathbf{e}_j \right\rangle}{4\pi N\rho^* r^2} \tag{1}$$

discriminates between side-by-side and nose-to-tail conformations of neighboring particles. $h_{110}(r)$ was measured in canonical MC simulations of $N=128$ CHDs in the vapor and liquid phases near coexistence at relative temperature $0.9\tau_c^d$. For comparison, simulations of DHSs were also carried out at comparable densities, and at a temperature of $\tau^d=0.138$, approximately 0.9 times the critical temperature determined from Fig. 3(a). Figures 4(a) and 4(b) show $h_{110}(r)$ in vapor and liquid phases of CHD systems with $d/\sigma=1$ and $d/\sigma=0.1$ and of the DHS system. To aid a comparison, the abscissas are scaled by the separation of two nose-to-tail CHDs at contact. In both the vapor and liquid phases of the system with $d/\sigma=1$, $h_{110}(r)$ is large and negative close to the side-by-side contact separation σ, reflecting the antiparallel alignment of the dipoles. Correlations die off rapidly beyond that distance. By contrast, the system with $d/\sigma=0.1$ exhibits pronounced correlations between parallel dipoles at integer values of the nose-to-tail contact separation $\sigma+d$, reflecting chaining; in the vapor phase, the negative "blip" at $r\lesssim\sigma+d$ arises from rare instances of the side-by-side conformation. The DHS results are qualitatively similar, although the nose-to-tail correlations are more pronounced. This demonstrates that the CHD model with $d/\sigma=0.1$ sports the characteristic structural features of the DHS fluid.

A comparison of structures can also be made in reciprocal space. The static structure factor is $S(\mathbf{q})=(1/N)\langle\rho(\mathbf{q})\rho(-\mathbf{q})\rangle$ where $\rho(\mathbf{q})=\Sigma_j^N \exp(-i\mathbf{q}\cdot\mathbf{r}_j)$ is a Fourier component of the density, and $\mathbf{q}$ is a wave vector commensurate with the periodic boundary conditions; in isotropic fluids, contributions with $|\mathbf{q}|=q$ can be averaged. Simulation results for low- and high-density phases are shown in Figs. 4(c) and 4(d), respectively. $S(q)$ in the CHD system with $d/\sigma=0.1$ is al-

most identical to that in the DHS fluid at the same density and at the same relative temperature, provided that the wave vectors are scaled by the nose-to-tail separation $(\sigma+d)$: features at $q(\sigma+d)\simeq 2\pi$ are due to near neighbors in the nose-to-tail conformation; in the vapor phases, the low wave vector "divergence" of $S(q)$ signals aggregation.[4] By contrast, there are clear differences between the results for the CHD system with $d/\sigma=1$ and those for DHSs. In the liquid, the position of the first major peak in $S(q)$ $(q\sigma\simeq 4.5)$ corresponds to a real-space separation of $2\pi/q\simeq 1.4\sigma$. This separation may correspond to the orientationally averaged distance of closest approach for two dumbbells, which would signal the presence of nose-to-tail and side-by-side conformations.

Tlusty and Safran have put forward a mechanism of dipole-driven coexistence based on not only the density difference between the coexisting phases but also the topologies of the aggregates in the coexisting phases.[21] The low-density chainlike phase is characterized by "end" defects, particles at the ends of chains with only one near neighbor. The high-density "network" phase is characterized by branching points, particles with three near neighbors. To explore this possibility, the fractions of particles with n near neighbors x_n have been calculated: x_1 and x_3 signal end and "Y" defects, respectively. Two particles were assigned as near neighbors if any two spheres on different particles were within a distance 1.1σ. In the CHD system with $d/\sigma=0.1$, the results for coexisting vapor and liquid phases at relative temperature $0.9\tau_c^d$ are $\{x_1=0.42, x_3=0.02\}$ and $\{x_1=0.17, x_3=0.39\}$, respectively. These are to be compared with results for the DHS system at the same densities and relative temperature $0.9\tau_c^d$, $\{x_1=0.14, x_3=0.01\}$ in the vapor and $\{x_1=0.08, x_3=0.34\}$ in the liquid. Hence, the simulation results are broadly in line with the scenario proposed by Tlusty and Safran: the dilute phase is rich in end defects, while the dense phase is rich in Y defects.

In summary, vapor-liquid coexistence in CHD fluids shows a crossover between ionic and dipolar regimes. An extrapolation of the results to the DHS limit yields reduced critical parameters of $\tau_c^d\simeq 0.153$ and $\rho_c^*\simeq 0.1$. It would be interesting to see if a robust theory can be developed to tackle such strongly correlated dipolar systems, perhaps as an extension to those developed for ionic fluids.[22,23]

The support of the UK Engineering and Physical Sciences Research Council (Grant No. EP/D002656/1) is gratefully acknowledged.

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[24] The near-critical data are not suitable for fitting the leading correction-to-scaling term $\propto t^{\beta+\Delta}$ with any confidence. Apparent critical parameters vary by a few percent if classical or fitted effective exponents are used. Ising-exponent fits are sufficient to demonstrate the existence of the transition and the crossover between ionic and dipolar regimes.